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(19) (CA) **CANADIAN PATENT** (12)

(54) Perfluoroalkyl-Sulfone Group Containing Acrylates and Methacrylates, a Process for their Production and their Use

(72) Kleiner, Eduard , U.S.A.
Karydas, Athanasios , U.S.A.

(73) Ciba-Geigy AG , Switzerland

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Perfluoroalkyl-Sulfone Group Containing Acrylates and Methacrylates, a process for their production and their use.

The instant invention relates to new and useful perfluoroalkyl sulfone group containing acrylate and methacrylate monomers, polymers thereof, and their use in rendering cellulosic, natural, and synthetic polyamide and polyester materials hydrophobic, oleophobic and dry soil resistant.

It is a further objective of this invention to provide a simple economic method of preparing such acrylate and methacrylate monomers.

Various structurally divergent perfluoroalkyl acrylate and methacrylate monomers are known as described in U.S. 2,642,416, 3,102,103, 3,282,905, 3,544,663, 3,655,732, and 4,060, 681 and in DE-A-2 052 579. However, their structure is different from those of the instant invention, and such prior-art preparations invariably entail cumbersome multistep techniques with consequent losses of the costly fluorochemical. Perfluoroalkyloxyperfluoralkyl acrylate and methacrylate monomers, having a thioether linkage, are described in US Patent 3,763, 116.

The perfluoroalkyl-containing acrylate and methacrylate monomers of the instant invention are represented by the formula I

$$R_f(CH_2)_nSO_2(CH_2)_mO_2C-\overset{R}{\overset{|}{C}}=CH_2 \qquad (I),$$

*

wherein

R_f is perfluoroalkyl or perfluoroalkoxy substituted perfluoroalkyl;

R is hydrogen or methyl,

n is 2-20,

m is 2-20.

The R_f group can contain up to 18 carbon atoms, preferably from 3 to 18 carbon atoms, especially from 6 to 16 carbon atoms and most preferably from 6 to 12 carbon atoms. The R_f group may be straight or branched chain. The R_f group may advantageously be in the form of a mixture of perfluoroalkyl, having a different number of carbon atoms.

The R group is preferably methyl.

In formula I, n and m are preferably 2 to 5, most preferably n is 2 and m is 2 to 4. Most advantageously m is 3.

The compounds of formula I are prepared by a variety of means all of which involve reaction of the intermediates of formula (II)

$$R_f(CH_2)_nSO_2(CH_2)_mOH \qquad (II)$$

with compounds of formula (III)

$$CH_2{=}CR{-}CO{-}Z \qquad (III),$$

where Z is methoxy, hydroxy or halo, by esterification or transesterification techniques all of which are well known in the art. For example, the reaction between the compounds of formula II and III can be conducted at a reaction temperature between about 20 and about 100°C in the presence of an inert diluent, such as tetrahydrofuran, dioxane, di-n-propyl ether and the like, in the presence or absence of a base, such as a tertiary lower alkyl amine,

such as trimethylamine or triethylamine, especially where Z is halo, in order to remove the acidic by-product and force the reaction to completion. If desired, an excess of the compound of formula III can be present over that required by stoichiometry in order to force the reaction to completion. The desired reaction product of formula I can be isolated by conventional means known in the art, such as precipitation, and the product purified if desired, e.g., by washing with water or a lower alkanol, such as methanol.

In order to obtain those compounds of formula (II) the thioether alcohol of formula (IV)

$$R_f(CH_2)_nS(CH_2)_mOH \qquad (IV)$$

is oxidized with an oxidizing agent. Suitable oxidizing agents include hydrogen peroxide in an organic acid medium, such as acetic acid. The reaction is conducted at a temperature of up to 100°C until the thioether alcohol is converted to the corresponding sulfone. In general, elevated temperatures, e.g. between about 50°C and 100°C, favor the formation of the corresponding sulfones. Moreover, a substantial excess of peroxide generally favors the formation of sulfones.

The alcohols of formula IV are known or can easily be prepared from known compounds by methods known per se. Thus, for example, the alcohols of formula IV can easily be prepared by reacting a mercaptan of formula (V),

$$R_f(CH_2)_nSH \qquad (V)$$

with either a haloalkanol of the formula (VI),

$$X(CH_2)_mOH \qquad (VI),$$

where X is halogen and m is as defined above, or an unsaturated alcohol of the formula (VII)

$$CH_2=CH(CH_2)_{m'-2}OH \qquad (VII),$$

wherein m' is 3-20.

The reaction between (V) and (VI) can easily be performed by reacting stochiometric amounts of each in presence of a base to remove the acid halide (HX) formed, in the presenc or absence of an inert solvent, at a reaction temperature between 30°C and 120°C, and removing the by-product salt, e.g. by washing with water. Suitable bases include alkali metal hydroxides and carbonates, alkaline earth metal hydroxides and carbamates and amines such as trimethylamine or pyridine. Sufficient base should be added during the course of the reaction to react with all hydrogen halide formed. Where employed, suitable inert solvents include toluene, tetrahydrofuran, dimethylsulfoxide, lower alkanols and the like.

In reacting the mercaptan of formula (V) with an unsaturated alcohol of formula (VII) to obtain the corresponding alcohol of formula (IV), the simple addition reaction is conveniently conducted in the presence of a free radical initiator, such as an azo-type free-radical initiator, for example 2,2'-azobis-(2,4-dimethylvaleronitrile), in the presence or absence of an inert solvent such as tetrahydrofuran, methyl ethyl ketone, dimethylsulfoxide or the like, at a reaction temperature between about 30° and 100°C.

Perfluoroalkyl thiols of formula (V) are well documented in the prior art. Thus, U.S. Patent 3,655,732 discloses mercaptans of formula R_f—R_1—SH where R_1 is alkylene of 1 to 16 carbon atoms and R_f is perfluoroalkyl and teaches that halides of formula R_f—R_1-halogen are well known; reaction of R_fI with ethylene under free-radical conditions give $R_f(CH_2CH_2)_aI$ while reaction of R_fCH_2I with ethylene gives $R_fCH_2(CH_2CH_2)_aI$ as is further taught in U.S. Patents 3,088,849; 3,145,222; 2,965,659 and 2,972,638.

U.S. Patent 3,544,663 teaches that the mercaptan $R_fCH_2CH_2SH$ where R_f is perfluoroalkyl of 5 to 13 carbon atoms, can be prepared by reacting the perfluoroalkyl alkylene iodide with thiourea or by adding H_2S to a perfluoroalkyl substituted ethylene (R_f—$CH{=}CH_2$), which in turn can be prepared by dehydrohalogenation of the halide R_f—CH_2CH_2—halogen.

The reaction of the iodide R_f—R_1—I with thiourea followed by hydrolysis to obtain the mercaptan R_f—R_1—SH is the preferred synthetic route and the reaction is applicable to both linear and branched chain iodides. Many useful perfluoroalkoxyalkyl iodides are described in published Australian Application 36 868 of general formula

$$(CF_3)_2CFOCF_2CF_2(CH_2CH_2)_pI\ ,$$

wherein

p is 1-3.

The instant α,β-unsaturated ester monomers of formula (I) are very reactive and have a strong tendency to form homo- or copolymers.

The polymerization of the R_f-acrylate and R_f-methacrylate monomers is analogous to the polymerization of such monomers as described in Houben-Weyl, Methoden der Organischen Chemie, Vol. 14/1, p 1044-1047, (Georg Thieme Verlag, Stuttgart, 1961) or C. E. Schidknecht, Vinyl and Related Polymers, p 179-255 (John Wiley and Sons Inc., New York 1952).

Generally polymerization may be carried out in bulk, solution, suspension or emulsion. Solution and emulsion polymerization are preferred.

In emulsion polymerization, the monomer or monomers to be polymerized are emulsified together in a water solution of a surface active agent to a given monomer concentration of from about 5 % to

about 50 %. Usually the temperature is raised to between 40°C and 70°C to effect polymerization in the presence of an added catalyst. A suitable catalyst may be of any one of the commonly known agents for initiating the polymerization of an ethylenically unsaturated compound. The concentration of the catalyst for the polymerization is usually between 0.1 % and 2 % based upon the weight of the monomers.

Suitable surfactants or emulsifying agents include cationic, anionic or non-ionic types. Since the cationic and non-ionic types can be used in most textile treating baths, they are preferred. The hydrophobic portion of the surfactant may be hydrocarbon or fluorinated hydrocarbon.

Suitable surfactants or emulsifying agents include, for example, non-ionic surfactants, in which the hydrophilic group is a poly-(ethoxy) group and the hydrophobic portion is either a hydrocarbon or a fluorocarbon group such as the ethylene oxide condensates of alkyl phenols, alkanols, alkylamines, alkyl thiols, alkylcarboxylic acids, fluoroalkyl carboxylic acids, fluoroalkyl amines and the like.

Suitable cationic surfactants include for example, quaternary ammonium salts or amine salts containing at least one long chain alkyl, fluoroalkyl, or high alkyl substituted benzene or naphthalene group to provide the hydrophobic portion.

Polymerization is preferably carried out for a reaction period adjusted to obtain essentially quantitative conversion of the fluorinated monomer. The optimum reaction time will depend upon the catalyst used and the polymerization temperature and other conditions, but will generally be in the range of from 0.5 to 24 hours.

The polymerization temperature will depend upon the catalyst chosen. In the case of emulsion polymerization in aqueous media, it will generally be in the range of from 20°C to 90°C. The polymerization is generally most conveniently and preferably carried out at atmospheric pressure wherever possible.

In solution polymerization, the monomer or monomers are dissolved in a suitable solvent such as tetrahydrofuran or fluorinated solvents, for example hexafluoroxylene, trifluorotoluene or mixtures thereof with acetone and/or ethylacetate and polymerized in a reaction vessel using initiators such as azobisisobutyronitrile or other azo initiators at concentrations of 0.1 to 2.0 % at 40°-100°C under nitrogen.

The monomers of formula I may be homopolymerized or co-polymerized with conventional, preferably non-fluorinated, monomers. The conventional monomers may be hydrophilic or hydrophobic or mixtures thereof. In order to impart soil release properties on textile materials, hydrophilic comonomers are advantageously employed. Where both hydrophobic and oleophobic properties are desired, the conventional comonomers are advantageously primarily hydrophobic in character for optimum results. While the amount of the monomer of formula I used in copolymerization with the conventional comonomers can vary widely, depending upon the amount of oleophobicity, and optionally hydrophobicity, desired in the final polymeric finish, advantageously at least about 10 weight percent up to about less than 100 weight percent, preferably between about 50 to 99.9, most preferably between about 65 to 90 weight percent of a monomer of formula I, or mixture thereof, is used per unit weight of conventional comonomers - monomer of formula I blend.

Comonomers useful in the preparation of copolymers of the novel R_f monomers include, without limitation:

Ethylene, and chloro-, fluoro-, amido- and cyano-derivatives of ethylene such as vinyl chloride, vinylidene chloride, vinyl fluoride, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide and N,N-dimethylacrylamide, tetrafluoroethylene, hexafluoropropylene; acrylate and methacrylate monomers, particularly those with 1 to 18 carbon atoms in the ester group such as n-propyl methacrylate, 2-methyl cyclohexyl methacrylate, methyl methacrylate, t-butyl methacrylate, n-butyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 3-methylpentyl acrylate, octyl acrylate, tetradecyl acrylate, s-butyl acrylate, 2-ethylhexylacrylate, 2-methoxyethyl acrylate, and phenyl acrylate; dienes, particularly 1,3-butadiene, isoprene, and chloroprene, 2-fluorobutadiene, 1,1,3-trifluorobutadiene, 1,1,2,3-tetrafluoro butadiene, 1,1,2-trifluoro-3,4-dichlorbutadiene and tri- and pentafluoro butadiene and isoprene; nitrogen vinyl monomers such as vinyl pyridine, N-vinylamides, vinyl succinimide, vinyl pyrrolidone, N-vinyl carbazole and the like; styrene and related monomers which copolymerize readily with the novel esters of this invention such as o-methylstyrene, p-methylstyrene, 3,4-dimethyl styrene, m-ethyl styrene, 2,5-diethyl styrene; vinyl esters, e.g. vinyl acetate; vinyl esters of substituted acids, such as for example, vinyl methoxyacetate, vinyl trimethylacetate, vinyl isobutyrate, isopropenyl butyrate, vinyl lactate, vinyl caprylate, vinyl pelargonate, vinyl myristate, vinyl oleate and vinyl linoleate; vinyl esters of aromatic acids, such as vinyl benzoate.

Straight and branched chain α-olefins with up to 10 carbon atoms in the side chain are useful as comonomers. Propylene, butylene and isobutylene are preferred α-olefins useful as comonomers with the novel fluoro monomers of the present invention.

Also useful as comonomers with some of the novel monomers of the present invention are vinyl monomers which contain perfluorinated side chains. Examples of such perfluorinated monomers are vinyl esters containing fluorinated alkyl groups disclosed in U.S. Patent Nos. 2,592,069 and 2,436,144. Other useful monomers are acrylates

and methacrylates and derivatives thereof such as those disclosed in U.S. Patent Nos. 2,628,958; 3,256,230; 2,839,513; 3,282,905; 3,252,932 and 3,304,278.

As mentioned, it may also be desirable to include a minor amount of other reactive comonomers e.g. in order to improve the wash and dry-clean properties of the novel textile finishes obtained according to the practice of this invention. Such monomers act as cross-linking agents during the curing operation and are generally employed in amounts of 0.01 % to 5 %, preferably 0.1 % to 2 % by weight, based on the weight of the comonomers.

Reactive monomers which may be included are by way of illustration: acrylic acid, methacrylic acid, acrylamide, N-methylolacrylamide, 2-hydroxyethyl methacrylate or acrylate, hydroxypropyl acrylate or methacrylate, and t-butylaminoethyl methacrylate, and glycidyl methacrylate. Of the foregoing, N-methylolacrylamide and 2-hydroxyethyl methacrylate are preferred.

Coatings of the homopolymers and copolymers according to the instant invention can be prepared and applied from solvent solutions or from aqueous emulsions. Suitable solvents are fluoroalkanes, fluorochloroalkanes, fluoroalkyl substituted aromatics, alkyl esters of perfluoroalkanoic acids, chlorinated alkanes or aromatics, hydrocarbon aromatics, ketones, esters and ethers.

Especially useful as solvents are the fluorinated liquids, and especially α,α,α-trifluorotoluene, otherwise known as benzotrifluoride, hexafluoroxylene and mixtures of these with ethyl acetate or acetone and the like. Concentrations of the fluorinated polymers of the instant invention in solvent to provide coatings with effective oil and water repellency properties will generally be of the order of 0.01 to 10 % and preferably from 0.1 to 2.0 % by weight. Blends of the emulsions of the polymers of this invention with blended emulsions of other polymers and copolymers are particularly useful in textile finishes. The polymer and copolymers are

generally of a non-fluorinated type; however, as indicated below other fluorinated polymers and copolymers may be used if desired. Nonfluorinated polymers useful in such blends, include for example, but without limitation, polymers and copolymers of alkyl acrylates and alkyl methacrylates, such as methyl methacrylate, ethyl methacrylate, hexyl methacrylate, and n-octyl methacrylate. A particularly suitable polymer is poly-n-octyl methacrylate. Also, useful are polymers and copolymers of acrylic acid, methacrylic acid, styrene, alkyl styrene, butadiene, 2-methyl-1,3-butadiene, 2-chloro-1,3-butadiene, polymers and copolymers of vinyl esters such as vinyl acetate, vinyl butyrate, vinyl laurate, vinyl stearate, vinyl 2-ethyl-hexanoate; polymers and copolymers of vinyl halides and vinylidene halides, such as vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride, polymers and copolymers of allyl esters such as allyl propionate or allyl caprylate, polymers and copolymers of vinyl ketones, such as methyl vinyl ether, cetyl vinyl ether, and the like; polymers and copolymers of acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, N-isopropyl acrylamide, and methacrylonitrile.

The polymers of this invention possess desirable oil repellency and dry soil resistant properties. A useful manner of measuring the relative ratings of the polymers is by oil and water repellency and dry soil resistance ratings. In the examples the following test procedures are used:

The AATCC oil rating is determined according to Standard Test Method 118-1966 T of the American Association of Textile Chemists and Colorists. Ratings are given from 0 (minimum) to 8 (maximum). A commonly accepted level on soil repellent fabrics in the U.S. is an oil repellency of 4.

Another oil repellency method is the 3-M Oil Test procedure of Grajek and Peterson, Textile Research Journal, April 1962, p. 323.

The AATCC water spray test rating is determined according to Standard Test Method 22-1966 of the American Association of Textile Chemists and Colorists XXVII, 1961, P. 1952 (also designated ASTM-D-583-58). Ratings are given from 0 (minimum) to 100 (maximum).

The dry soil resistance is determined according to an accelerated Bag Method which is described below:

Treated and untreated fabrics are shaken in a plastic bag with standard dry soil for a specified time. Excess soil is then removed from the fabrics under controlled conditions and the soiled fabrics then are evaluated visually using the "Competitive Dry Soil Rating" chart. Ratings are given from 0 (minimum) to 100 (maximum).

The polymers of the invention are dissolved in 1,1,1-trichloroethane. The concentration of the solutions is 1 weight percent. The solutions are applied to fabric by a padding process and they are evaluated after air drying and after curing in a hot oven at 150° for 3 minutes.

For a clearer understanding of the invention, the following specific examples are given. These examples are intended to be merely illustrative of the invention and not a limitation thereof. Unless oterhwise specified all parts are by weight.

Example 1

Allyl alcohol (44.4 g, 0.76 moles) and $C_6F_{13}CH_2CH_2SH$ (190 g, 0.5 moles) are mixed under nitrogen and the solution is heated to 55°C. Azo bis (2,4-dimethylvaleronitrile), (1.4 g, 0.01 moles) in methyl ethyl ketone (15 mol) is added over a 50 minute period. After the addition is complete the solution is stirred at 55°C for one hour and acetic acid (200 g) is added. The resulting solution is heated to 70°C and a solution of hydrogen peroxide in water (137 g of a 30 % solution) is added at such a rate that the solution temperature does not exceed 85°C. After the addition is complete the solution is heated to 90°C for 45 minutes, cooled, and poured into

two liters of cold, rapidly stirring water. A white solid precipitates and is collected by filtration. Successive washings with 2 % NaOH and water followed by drying give 211 g (94 % yield) of a product with the structure

$C_6F_{13}CH_2CH_2SO_2CH_2CH_2CH_2OH$.

NMR: 1.80 ppm, multiplet, 2H, $CH_2\underline{CH_2}CH\ OH$;
2.40-3.12 ppm, multiplet, 2H, $C_6F_{13}\underline{CH_2}CH$;
3.49 ppm, two triplets, 4H, $\underline{CH_2}SO_2\underline{CH_2}$;
3.99 ppm, triplet, 2H, $CH_2\underline{CH_2}OH$.

Analysis: Calculated: 28.1 % C, 2.3 % H, 52.6 % F, 6.8 % S
Found: 28.2 % C, 2.5 % H, 52.8 % F, 6.8 % S

m.p. 178-183°C.

Example 2

Following the procedure from example 1, using $C_8F_{17}CH_2CH_2SH$, an alcohol of the formula

$C_8F_{17}CH_2CH_2SO_2CH_2CH_2CH_2OH$

is obtained in 91 % yield.

NMR 1.80 ppm, multiplet, 2H, $\underline{CH_2}CH_2CH_2OH$;
2.40-3.12 ppm, multiplet, 2H, $C_6F_{13}\underline{CH_2}CH$;
3.49 ppm, two triplets, 4H, $\underline{CH_2}SO_2\underline{CH_2}$;
3:99 ppm, triplet, 2H, $CH_2\underline{CH_2}OH$.

Analysis: Calculated: 27.4 % C, 1.9 % H, 56.7 % F
Found: 27.0 % C, 1.8 % H, 56.6 % F

m.p. 182-185°C.

Example 3

Following the procedure from example 1, using $R_fCH_2CH_2SH$, an alcohol of the formula

$$R_fCH_2CH_2SO_2CH_2CH_2CH_2OH \text{ wherein}$$

R_f is 6 % C_8F_{17}, 64 % $C_{10}F_{21}$, 25 % $C_{12}F_{25}$, 5 % $C_{14}F_{29}$,

is obtained in 95 % yield.

NMR:	1.80 ppm, multiplet, 2H, $\underline{CH_2}CH_2CH_2OH$;
	2.40-3.12 ppm, multiplet, 2H, $C_6F_{13}\underline{CH_2}CH$;
	3.49 ppm, two triplets, 4H, $\underline{CH_2}SO_2\underline{CH_2}$;
	3.99 ppm, triplet, 2H, $CH_2\underline{CH_2}OH$.
Analysis:	Calculated: 26.1 % C, 1.6 % H, 58.0 % F, 4.7 % S
	Found: 26.1 % C, 1.5 % H, 59.4 % F, 4.6 % S
m.p.	188-192°C.

Example 4

Triethylamine (21.1 g, 0.209 moles) and $C_6F_{13}CH_2CH_2SO_2CH_2CH_2CH_2OH$ (89.0 g, 0.189 moles) are dissolved in dry tetrahydrofuran (1200 g) and the solution is stirred at room temperature under nitrogen. Methacryloyl chloride (21.8 g, 0.209 moles) is added dropwise and the solution is heated to reflux overnight. A precipitate formed and the solution is filtered and the solvent is evaporated. The resulting solid is washed with methanol to give a product with the structure

$$CH_2{=}\overset{\overset{\large CH_3}{|}}{C}{-}CO_2CH_2CH_2CH_2SO_2CH_2CH_2C_6F_{13}$$

in 70 % yield.

NMR: 1.87 ppm, singlet, 3H, $CH_2{=}C(CH_3){-}$

1.90-2.75 ppm, multiplet, 4H, $CH_2\underline{CH_2}CH_2OH$, $C_6F_{13}\underline{CH_2}CH_2{-}$;

3.37 ppm, multiplet, 4H, $\underline{CH_2}SO_2\underline{CH_2}$;

4.10 ppm, triplet, 2H, $CH_2\underline{CH_2}O{-}$;

5.65, 6.02 ppm, singlets with fine splitting, 2H, $\underline{CH_2}{=}C(CH_3){-}$.

Analysis: Calculated: 33.5 % C, 2.8 % H, 45.9 % F

Found: 33.1 % C, 2.7 % H, 46.8 % F

m.p. 105.5-106°C.

Example 5

Methyl methacrylate (350 g, 3.5 moles), 2,6-di-t-butyl-4-methylphenol (2.4 g, 0.7 % by weight of methyl methacrylate) and $C_8F_{17}CH_2CH_2SO_2CH_2CH_2CH_2OH$ (50.0 g, 0.088 moles) are mixed under nitrogen. The solution is refluxed under a 45 cm fractionating column equipped with Dean-Stark trap and condenser in order to remove all traces of water. As the head temperature rises to 100°C, 60 ml of the methyl methacrylate/water azeotrope is removed and the reaction is replenished with an additional 50 ml of methyl methacrylate. Tetraisopropyl titanate, (9.0 g, 0.03 moles) is then added and the resulting solution is heated under reflux (head temperature 100°C) until the head temperature dropped several degrees. The heat source is removed, 32 ml methyl methacrylate/methanol azeotrope is collected and the excess methyl methacrylate is removed under vacuum. The remaining slurry is stirred and partially dissolved in tetrahydrofuran and filtered to remove the insoluble titanate catalyst. Tetrahydrofuran is removed under vacuum to give 53.01 g (94 % yield) of a product with the structure

$$C_8F_{17}CH_2CH_2SO_2CH_2CH_2CH_2O_2CC(CH_3){=}CH_2.$$

NMR: 1.87 ppm, singlet, 3H, $CH_2=\overset{CH_3}{\underline{C}}-$
1.90-2.75 ppm, multiplet, 4H; $CH_2\underline{CH_2}CH_2OH$, $C_6F_{13}\underline{CH_2}CH_2-$;
3.37 ppm, multiplet, 4H, $\underline{CH_2}SO_2\underline{CH_2}$;
4.18 ppm, triplet, 2H, $CH_2\underline{CH_2}O-$;
5.65, 6.02 ppm, singlets with fine splitting, $\underline{CH_2}=\overset{CH_3}{C}-$

Analysis: Calculated: 32.0 % C, 2.4 % H, 50.6 % F, 5.0 % S
Found: 31.8 % C, 2.1 % H, 50.7 % F, 5.4 % S.

Example 6

Following the procedure from example 4 and using the alcohol $R_fCH_2CH_2SO_2CH_2CH_2CH_2OH$ obtained in example 3, a methacrylate with the structure

$$R_fCH_2CH_2SO_2CH_2CH_2CH_2O_2C-\overset{CH_3}{C}=CH_2,$$

wherein R_f is 6 % C_8F_{17}, 64 % $C_{20}F_{21}$, 25 % $C_{12}F_{25}$, 5 % $C_{14}F_{29}$, is obtained in 75 % yield.

NMR: 1.80 ppm, singlet, 3H, $CH_2=\overset{\underline{CH_3}}{C}-$
1.90-2.75 ppm, multiplet, 4H, $CH_2\underline{CH_2}CH_2OH$, $C_6F_{13}\underline{CH_2}CH_2-$;
3.37 ppm, multiplet, 4H, $CH_2SO_2CH_2$;
4.18 ppm, triplet, 2H, $CH_2\underline{CH_2}O-$;
5.65, 6.02 ppm, singlets with fine splitting, 2H, $\underline{CH_2}=\overset{CH_3}{C}-$

Analysis: Calculated: 30.3 % C, 2.0 % H, 53.1 % F, 4.3 % S
Found: 30.6 % C, 2.2 % H, 53.3 % F, 4.4 % S.

Examples 7-15

The fluorinated methacrylates described in Examples 4-6 are used to synthesize homopolymers and copolymers. The monomers are dissolved in tetrahydrofuran, azo initiator is added and the solutions are placed in ampules which are evacuated and sealed. Polymerizations are conducted at 100°C overnight in an agitating bath.

	Polymers of $CH_2{=}C(CH_3){-}CO_2(CH_2)_3SO_2(CH_2)_2R_f$ (A) and $CH_2{=}C(R){-}CO_2R_h$ (B)				
Example	R_f	% A	R	R_h	% B
7	C_8F_{17}	100	-	-	-
8	*	100	-	-	-
9	C_8C_{17}	80	CH_3	$C_{13}H_{17}$	20
10	*	90	CH_3	$C_{13}H_{17}$	10
11	*	80	CH_3	$C_{13}H_{17}$	20
12	*	70	CH_3	$C_{13}H_{17}$	30
13	C_8F_{17}	90	H	2 ethyl hexyl	10
14	C_8F_{17}	80	H	2 ethyl hexyl	20
15	C_8F_{17}	70	H	2 ethyl hexyl	30

* R_f is a mixture consisting of 6 % C_8F_{17}, 64 % $C_{10}F_{21}$, 25 % $C_{12}F_{25}$ and 5 % $C_{14}F_{29}$

Example 16

The polymers described in the above examples are applied to 100 % Nylon fabric at 0.1 % fluorine based on the weight of the fabric. Results are summarized in Table 1.

<u>Table 1</u>

Textile Application Data for Copolymers of

$$CH_2=\overset{CH_3}{\overset{|}{C}}-CO_2(CH_2)_3SO_2(CH_2)_2R_f \quad \text{and} \quad CH_2=\overset{R}{\overset{|}{C}}-CO_2R_h$$

Polymer from Example	Air Dried *			Oven Dried 150°C 5 min.*		
	A² Oil	A² Spray	Dry Soil	A² Oil	A² Spray	Dry Soil
7	5	70	90	5-6	70	90
9	3	90	80	5	100	90
13	5	80	80-90	5	90	90-100
14	4-5	80	90	4-5	80	90-100
15	5	70	80	5-6	70	90

* A^2 means AATCC

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A perfluoroalkyl containing acrylate or methacrylate derivative of the formula I

$$R_f(CH_2)_nSO_2(CH_2)_mO_2C-\overset{\displaystyle R}{\overset{|}{C}}=CH_2 \qquad \text{(I)},$$

wherein

R_f is perfluoroalkyl of up to 18 carbon atoms, or perfluoroalkoxy substituted perfluoroalkyl of up to 18 carbon atoms;

n is 2-20;

m is 2-20; and

R is hydrogen or methyl.

2. A compound according to claim 1, wherein R is methyl.

3. A compound according to claim 1, wherein n is 2-5 and m is 2-5.

4. A compound according to claim 3, wherein n is 2 and m is 2-4.

5. A compound according to claim 1, wherein R_f contains from 3 to 18 carbon atoms.

6. A compound according to claim 1 wherein m is 3.

7. An oleophobic copolymer of the monomer of formula (I) according to claim 1 and at least one comonomer, wherein the monomer of formula (I) is employed in an amount of between about 50 to 99.9 weight percent of the copolymer.

8. A method of rendering a cellulosic, natural or synthetic polyamide or polyester substrate hydrophobic, comprising forming a coating of a polymer according to claim 7 on the surface of said substrate.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS

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Perfluoroalkyl-Sulfone Group Containing Acrylates and Methacrylates, a process for their production and their use.

Abstract of the Disclosure

Perfluoroalkyl containing acrylate and methacrylate monomer derivatives of the formula I

$$R_f(CH_2)_nSO_2(CH_2)_mO_2C{-}\overset{R}{\overset{|}{C}}{=}CH_2 \qquad (I),$$

wherein

R_f is perfluoroalkyl or perfluoroalkoxy substituted perfluoroalkyl,

R is hydrogen or methyl,

n is 2-20,

m is 2-20;

their preparation and their use in the preparation of hydrophobic, oleophobic and dry soil resistant finishes are disclosed.